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(54) MASS SPECTROMETRY DEVICE

MASSENSPEKTROMETRIEVORRICHTUNG

DISPOSITIF DE SPECTROMÉTRIE DE MASSE

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Description

Technical Field

[0001] The present invention relates to a mass spectrometer and a method of operating the same.

Background Art

[0002] An ionization using a plasma of corona discharge, glow discharge or the like is widely used in mass spectrometry in various fields. An explanation will be given as follows of how the ionization by the plasma has been carried out until this time.

[0003] Patent Literature 1 describes a method of carrying out an ionization by an atmospheric pressure chemical ionization method. According to the atmospheric pressure chemical ionization method, the ionization is carried out by corona discharge under an atmospheric pressure. A sample molecule is ionized by an ion molecular reaction with a primary ion which is generated by the corona discharge.

[0004] Patent Literature 2 describes a method of carrying out an ionization by glow discharge by introducing a sample into a vacuum chamber. A pressure in the vacuum chamber for carrying out the ionization is about 0.1 through 1 Torr (1 x 10 through 1×10^2 Pa) .

[0005] Patent Literature 3 describes a method of carrying out an ionization by a dielectric barrier discharge under an atmospheric pressure. In the dielectric barrier discharge, a low temperature plasma is generated by preventing an elevation of a temperature of a neutral gas or an ion in the plasma by interposing a dielectric between electrodes. According to Patent Literature 3, the plasma which is ejected from a probe under the atmospheric pressure is directly impinged on a sample to thereby carry out the ionization, and a generated ion is introduced to a mass spectrometer.

[0006] Nonpatent Literature 1 describes a method of carrying out an ionization by a dielectric barrier discharge which uses helium as a discharge gas in vacuum. According to the method described in Nonpatent Literature 1, a sample and helium are introduced into a vacuum chamber of a mass spectrometer by passing a capillary of a dielectric, and the sample is ionized by the dielectric barrier discharge at a vicinity of an outlet of the capillary on a side of the vacuum chamber. A flow rate of the gas which is introduced into the vacuum chamber is 25 ml/min, and a pumping speed of a pump which extracts the gas from the vacuum chamber is 300 L/s. Therefore, the vacuum chamber and the vicinity of the outlet of the capillary on the side of the vacuum chamber where the ionization occurs are maintained under a high degree of vacuum. There is strongly observed an atom ion which is produced by dissociating a molecule ion under a condition of Nonpatent Literature 1.

Citation List

Patent Literatures

[0007]

Patent Literature 1: US7,064,320
Patent Literature 2: US4,849,628
Patent Literature 3: WO2009/102766

[0008] US2005/121607A1 discloses a differential ion mobility spectrometer with the features in the preamble of present claim 1.

Nonpatent Literature

[0009] Nonpatent Literature 1: Analytical chemistry, 1998,70,513-518

Summary of Invention

Technical Problem

[0010] According to the atmospheric pressure chemical ionization described in Patent Literature 1, the ion which is generated under the atmospheric pressure is introduced to the mass spectrometer by passing the ion through an orifice or a capillary. Therefore, there poses a problem that a loss of ion occurs when the ion passes through the orifice or the capillary. Furthermore, there also poses a problem that a density of charged particles of the corona discharge which is used in the atmospheric pressure chemical ionization is lower than that of other plasmas, and therefore, a number of ions generated is small.

[0011] According to the ionization by the glow discharge under a reduced pressure which is described in Patent Literature 2 and Nonpatent Literature 1, there poses a problem that fragmentation of molecule ions occurs. When the fragmentation occurs, a mass spectrum becomes complicated, and it is difficult to analyze the spectrum.

[0012] According to the ionization method which uses the dielectric barrier discharge under the atmospheric pressure described in Patent Literature 3, similar to a case of an ionization source of the atmospheric pressure chemical ionization, the generated ion is introduced to the vacuum chamber by passing an orifice or a capillary, and therefore, there poses a problem that a sensitivity is low.

[0013] According to the method described in Nonpatent Literature 1, the fragmentation of ions is considerably promoted. However, Nonpatent Literature 1 does not describe a method of restraining the fragmentation.

Solution to Problem

[0014] In order to resolve the problem described

above, the mass spectrometer according to the present invention has the features defined in claim 1. The dependent claims relate to preferred embodiments.

[0015] There is provided other example of a mass spectrometer which is featured in including a first electrode, a second electrode, a dielectric portion provided between the first electrode and the second electrode and having an introducing portion and an extracting portion of a sample, a power source of superimposing an alternating current voltage at a frequency equal to or higher than 1 and equal to or lower than 300 kHz on one of the first electrode and the second electrode and ionizing the sample by a discharge generated between the first electrode and the second electrode, and a mass analyzing portion of analyzing an ion extracted from the extracting portion.

[0016] There is provided other example of a mass spectrometer which includes a first chamber including a first electrode, a second electrode, a dielectric portion provided between the first electrode and the second electrode, and an introducing portion and an extracting portion of a sample, a power source of superimposing an alternating current voltage on one of the first electrode and the second electrode and ionizing the sample by a discharge generated between the first electrode and the second electrode, and a second chamber including a mass spectrometer of analyzing an ion of the sample extracted from the extracting portion, the mass spectrometer being featured in that a pressure of the first chamber is higher than a pressure of the second chamber.

Advantageous Effects of Invention

[0017] According to the present invention, an ionization with inconsiderable fragmentation is realized highly sensitively.

Brief Description of Drawings

[0018]

Fig. 1 is a device configuring view of a first example useful to understand the invention.
Fig. 2 shows an ionization source of the first example.
Fig. 3 shows an ionization source of the first example.
Fig. 4 shows an ionization source of the first example.
Fig. 5 is an explanatory view of an effect.
Fig. 6 is an explanatory view of an effect.
Fig. 7 shows an ionization source of a second example useful to understand the invention.
Fig. 8 shows an ionization source of the embodiment.
Fig. 9 shows an ionization source of a third example useful to understand the invention.
Fig. 10 shows an ionization source of the third example.
Fig. 11 is a device configuring view of a fourth example useful to understand the invention.
Fig. 12 shows a reduced pressure chamber of the fourth example.
Fig. 13 shows a reduced pressure chamber of the fourth example.
Fig. 14 shows a reduced pressure chamber of the fourth example.
Fig. 15 shows an ionization source of a fifth example useful to understand the invention.

Description of Illustrative Examples and the Embodiment

First Example and Embodiment

[0019] Fig. 1 is a configuring view showing a mass spectrometer according to a first example useful to understand the present invention. A sample is introduced from an inlet of a capillary of an ionization source 1 along with air under an atmospheric pressure. The sample can also be mixed with a gas of nitrogen, helium, argon or the like other than air to be introduced into the capillary. When the capillary is heated, the sample or foreign matters can be prevented from being adsorbed to an inner wall of the capillary. An ion which is generated by the ionization source 1 is introduced into a first differential pumping chamber 2 of a vacuum chamber. The first differential pumping chamber 2 is maintained at about 1 through 1.0×10^4 Pa by exhausting the gas by a vacuum pump 51 of a rotary pump, a diaphragm pump or the like. The ion which is introduced into the first differential pumping chamber 2 is made to converge by a multipole ion guide 4, and is introduced into a second differential pumping chamber 3. The second differential pumping chamber 3 is maintained at about 10^{-4} Torr through 10^{-2} Torr (1×10^{-2} Pa through 1 Pa) by exhausting the gas by a vacuum pump 52. A mass spectrometry unit 5 and a detector 6 are installed in the second differential pumping chamber 3. Ions which are introduced into the second differential pumping chamber 3 are selected for respective m/z' by the mass spectrometry unit 5 of a quadrupole mass filter, an ion trap, a time-of-flight mass spectrometer or the like, and are detected by the detector 6 of an electron multiplier tube or the like. FT-ICR or the like may be used instead of the mass spectrometry unit 5 and the detector 6.

[0020] Fig. 2 shows a configuring view of the ionization source 1. (B) is a view viewing from a direction b of (A). The ionization source 1 consists of a dielectric capillary 10 which is configured by a dielectric of glass, plastic, ceramic, resin or the like, a first discharge electrode 11 which is inserted to an inner portion of the dielectric capillary, and a second discharge electrode 12 which is provided at an outer portion of the dielectric capillary. A dielectric barrier discharge is brought about between the second discharge electrode 12 and the first discharge electrode 11 via the dielectric capillary 10, and a plasma 100 is generated at an area which is interposed by the second discharge electrode 12 and the first discharge electrode 11. When a large discharge current flows substantially continuously in discharging, a plasma temper-

ature is elevated and a fragmentation is easy to occur. However, the dielectric which is disposed between the discharge electrodes is operated as a capacitor in the dielectric barrier discharge. It can therefore be prevented that the discharge current flows continuously and the plasma temperature is elevated. In Fig. 2(B), the second discharge electrode 12 is arranged to be shifted from a center axis of the dielectric capillary 10. Thereby, the first and the second discharge electrodes are further proximate to each other. Therefore, there is achieved an effect that the discharge is easy to be started.

[0021] The first discharge electrode may be a wire electrode as shown in Fig. 1, or a cylindrical electrode as shown in Fig. 4. Or, as shown in Fig. 8 and in line with the embodiment of the present invention, the dielectric capillary 10 and a conductor capillary 13 may be connected and the conductor capillary 13 may be used as the first discharge electrode. When the conductor capillary 13 is used, the capillary can be prevented from being charged up by the ion that is generated at the ionization source. On the other hand, a structure thereof becomes complicated since the capillaries having different materials are connected at a midway.

[0022] Although the materials of the first and the second discharge electrodes 11 and 12 and the conductor capillary 13 may be conductors, the service life of the electrodes is prolonged when the material uses a metal which is strong at corrosion of gold or the like.

[0023] The second discharge electrode 12 may only be brought into contact with a portion of an outer side of the dielectric capillary 10. However, the discharge occurs uniformly in a diameter direction of the dielectric capillary 10 by a structure in which the second discharge electrode 12 is brought into contact with a total of the dielectric capillary 10 as shown in Fig. 2. Therefore, the sample can efficiently be ionized.

[0024] An inner diameter of the dielectric capillary is typically 10 um through 1 cm, and a length thereof is typically about 0.1 through 1 m. The shorter the length of the dielectric capillary, and the larger the inner diameter, the more increased the conductance of the dielectric capillary, and the more increased the amount of a gas which is introduced to the mass spectrometer per constant period of time. The larger the conductance, the more increased the sensitivity of the mass spectrometer. On the other hand, the smaller the conductance, the more reduced the pumping speed of a pump which is necessary for maintaining the pressure of the second differential pumping portion 3 equal to or lower than an operable pressure of the mass spectrometry unit 5 and the detector 6, and a small-sized pump can be used.

[0025] There may be used a capillary in which an inner diameter of the capillary is changed at a midway as shown in Fig. 3. Here, when the inner diameter of the plasma is increased in an area where the plasma is generated, a time period during which an ion dwells in the plasma is prolonged, and an ion molecular reaction is easy to occur.

[0026] The shortest distance between the first discharge electrode 11 and the second discharge electrode 12 is typically about 1×10^{-4} through 1×10^{-1} m. The longer the distance between the first discharge electrode 11 and the second discharge electrode 12, the longer the time period during which a sample molecule exists in the plasma and the easier the ion molecule reaction occurs. On the other hand, the longer the distance between the first discharge electrode 11 and the second discharge electrode 12, the higher the voltage necessary for the discharge.

[0027] Fig. 5 shows a relationship between a break down voltage and a product of a pressure by a distance between discharge electrodes (pd product) with regard to air. The break down voltage becomes a minimum at a vicinity of 0.5 cm Torr, thereafter, the larger the pd product, the more increased the break down voltage. In a case where a discharge gas is air and a pressure thereof is 10 Torr (1.3×10^3 Pa), the discharge voltage is 1 kV at the distance between electrodes of 1 cm and about 4 kV at the distance between electrodes of 5 cm.

[0028] An AC voltage is superimposed from a power supply 50 on one of the first discharge electrode 11 and the second discharge electrode 12, and a DC voltage is superimposed on the other. The other electrode may be grounded instead of superimposing the DC voltage on the other electrode. Although in the following embodiments, a description is given in a case where an AC voltage is superimposed on the first discharge electrode 11, a similar effect can be achieved even in a case where the DC voltage (or the ground) is superimposed on the first discharge electrode 11, and the AC voltage is superimposed on the second discharge electrode 11.

[0029] The AC voltage generated at the power supply 50 may be of a rectangular wave or a sine wave. Typically, the superimposed voltage falls in a range of 0.5 through 10 kV and a frequency falls in a range of 1 through 300 kHz. Under a condition of a high frequency (100 through 300 kHz), a density of the plasma is increased, and therefore, although an ionization efficiency is high, the fragmentation is easy to occur. On the other hand, under a condition of a low frequency (1 through 20 kHz), the fragmentation is difficult to occur and also a molecule ion which is easy to be destructed can be detected. However, the ionization efficiency is lower than that in the case of the high frequency. Under a condition where the frequency falls in a range of 20 through 100 kHz, an intermediate property is shown.

[0030] When an amplitude of the voltage stays the same, the density of the plasma is higher in a case of using the rectangular wave. On the other hand, in a case of a high frequency, the voltage can be amplified by a coil in the sine wave. Therefore, there is achieved an advantage that the power supply is inexpensive. The frequency and the voltage of the AC voltage may be changed for respective ions of samples or measurement objects. For example, an inputted power is made to be high in a case of measuring a molecule which is difficult

to cause the fragmentation as in an inorganic substance ion or a case of measuring a fragment ion, and the inputted power is made to be low in a case of measuring a molecule ion which is easy to cause the fragmentation. Also, power consumption of the power supply 50 can be restrained when the power is controlled by providing a control mechanism of switching the voltage over time such that the ionization is carried out by superimposing the AC voltage only during a time period in which a sample is introduced, and the AC voltage is not superimposed during a time period in which the sample is not introduced.

[0031] According to the present invention, the ionization can be carried out highly sensitively while restraining the fragmentation by generating the plasma under a reduced pressure equal to or higher than 2 Torr (2.7 x 10^2 Pa) and equal to or lower than 300 Torr (400 x 10^2 Pa). When a pressure at a region of generating the plasma is higher than 300 Torr (400 x 10^2 Pa), the voltage which is necessary for starting the discharge becomes high, and there is a possibility of effecting an influence on generating the plasma. However, the stable plasma can be generated by making the pressure equal to or lower than 300 Torr (400 x 10^2 Pa). Fig. 6 shows a result of ionizing methyl salicylate by the configuration of the present example and plotting a pressure dependence of a signal intensity of an ion which is observed. The discharge gas is air, and a rectangular wave voltage superimposed on the first discharge electrode 11 is 2 $kV_{0\text{-}peak}$ at 15 kHz. A signal intensity of a protonated ion of methyl salicylate ([M+H]+, m/z 153) is increased at 4 Torr (5.3 x 10^2 Pa)or higher and is finally saturated. It seems that this is because the higher the pressure of the discharge gas, the easier the ion-molecule reaction occurs. The sensitivity of the molecule ion of the sample is low at 2 Torr (2.7 x 10^2 Pa) through 4 Torr (5.3 x 10^2 Pa). However, an amount of primary ions is larger than an amount of the sample molecule. Therefore, there is achieved an advantage that an influence of ion suppression is difficult to be effected. On the other hand, at 7 Torr (9.3 x 10^2 Pa) or higher, the molecule ion of the sample can be detected highly sensitively. At 4 through 7 Torr (5.3 x 10^2 to 9.3 x 10^2 Pa), an intermediate property thereof is shown. At 2 Torr (2.7 x 10^2 Pa) or lower, a molecule ion originated from methyl salicylate of a protonated ion or the like is hardly observed. This is because when the pressure of the discharge gas is low, a probability of impinging a high energy electron directly on the sample molecule is high, and the fragmentation is easy to occur.

[0032] A pressure at an inlet of the dielectric capillary 10 is the atmospheric pressure, and a pressure at an outlet thereof is a pressure of the first differential pumping chamber 2. Therefore, there is present a pressure gradient in an axial direction of the capillary. Therefore, a pressure at an area of generating the plasma can be adjusted by selecting a position of the area of generating the plasma 100 in the axial direction of the capillary. At this occasion, the smaller the pressure difference between the area of generating the plasma and the first differential pumping chamber 2, the larger the conductance between the region of generating the plasma and the first differential pumping chamber 2 can be made. The larger the conductance, the more the loss of ions by an influence of the space charge or a collision to the inner wall of the tube can be restrained, and an efficiency of introducing the ion to the first differential pumping chamber 2 is increased.

[0033] According to the present invention, the sample gas passes from the inlet of the capillary to the area of generating the plasma 100 in a state of a neutral gas. Therefore, the loss of ions by the influence of the space charge or the collision to the inner wall of the tube can be restrained, and the sample can be introduced into vacuum with a high efficiency. Also, the plasma is generated in a small area, and therefore, the plasma having the high density can be generated with low power consumption. According to the present invention, the fragmentation can be restrained while maintaining the stable discharge.

Second Example

[0034] Fig. 7 is a configuring view showing a mass spectrometer according to a second example useful to understand the present invention. A configuration other than the ionization source 1 is similar to that of the first example and an explanation thereof will be omitted. Also, an effect of a pressure at an area where the plasma 100 is generated, and an output voltage of the power source 50 are similar to those of the first example. The ionization source 1 is configured by the dielectric capillary 10 and two sheets or more of discharge electrodes 14 and 15. The discharge electrodes 14 and 15 are arranged to surround an outer side of the dielectric capillary 10. There are alternately arranged the first discharge electrodes 14 which are superimposed with an AC voltage from the power source 50 and the second discharge electrodes which are superimposed with a DC voltage therefrom. Conversely, the first discharge electrode 14 may be superimposed with the DC voltage and the second discharge electrode 15 may be superimposed with the AC voltage. Also, the discharge electrode may be grounded instead of superimposing the DC voltage thereon. The dielectric barrier discharge is caused between the first discharge electrode 14 and the second discharge electrode 15 by way of the dielectric capillary 10, and the plasma 100 is generated at an area between the first discharge electrode 14 and the second discharge electrode 15. An insulator 42 may be inserted between the first discharge electrode 14 and the second discharge electrode 15 in order to prevent a discharge on the outer side of the dielectric capillary 10. The discharge between the discharge electrodes 14 and 15 on the outer side of the capillary is difficult to be caused by installing the first discharge electrode 14 and the second discharge electrode 15 in the atmosphere. This is because in the air, the discharge voltage becomes high under an atmos-

pheric pressure in view of the relationship of Fig. 5.

[0035] Different from the configuration of the first example, it is not necessary to put the electrode at inside of the capillary where the sample passes. Therefore, a contamination of adhering the sample to the electrode or the like can be avoided. Also, a length of an area where the plasma is generated can be adjusted by changing numbers of the discharge electrodes while maintaining distances among the electrodes.

Third Example

[0036] Fig. 9 is a configuring view showing a mass spectrometer according to a third example useful to understand the present invention. (B) of the drawing is a view viewing (A) from a direction b. The configuration other than the ionization source 1 is similar to that of the first example and an explanation thereof will be omitted. Also, the effect of the pressure of the area where the plasma 100 is generated and the output voltage of the power source 50 are similar to those of the first example. The ionization source 1 is configured by the dielectric capillary 10, a first discharge electrode 40, and a second discharge electrode 41. One of the first discharge electrode 40 and the second discharge electrode 41 is supplied with an AC voltage from the power source 50, and the other is superimposed with a DC voltage or the grounded. A dielectric barrier discharge is caused between the first discharge electrode 40 and the second discharge electrode 41 by way of the dielectric capillary 10, and a plasma is generated at the region 100. The first discharge electrode 40 and the second discharge electrode 41 may be arranged on an inner side and an outer side of the dielectric capillary as shown in Fig. 9 or may be arranged on the outer side of the capillary as shown in Fig. 10. An insulator may be inserted between the electrodes in order to prevent a discharge.

[0037] In comparison with the configuration of the first example, the discharging electrodes are arranged such that a distance between the discharge electrodes stays constant without depending on a position in an axial direction of the capillary. Therefore, the plasma which is uniform in the axial direction can be configured. Also, when lengths of the first discharge electrode 40 and the second discharge electrodes 41 in the axial direction of the dielectric capillary are changed, a length of an area where the plasma is generated can be changed. Fourth Example

[0038] Fig. 11 is a configuring view showing the mass spectrometer according to a fourth example useful to understand the present invention. A neutral sample gas is introduced to a reduced pressure chamber 7 by passing an orifice 20. The reduced pressure chamber 7 is maintained under a reduced pressure condition of 5 Torr (6.7 x 10^2 Pa) or higher, and a plasma is generated by using a dielectric barrier discharge at inside of the reduced pressure chamber. The reduced pressure chamber 7 may be vacuumed by a vacuum pump 53.

[0039] The sample ion which is ionized at inside of the reduced pressure chamber is introduced from the first differential pumping chamber 2 by passing an orifice 21. The smaller the pressure difference between the reduced pressure chamber 7 and the first differential pumping chamber 2, the larger the conductance of the orifice 21 can be made. The larger the conductance, the higher the efficiency of introducing ions into the first differential pumping chamber 2. The effect of the pressure of the area where the plasma 100 is generated and the output voltage of the power source 50 are similar to those of the first example.

[0040] Figs. 12, 13, and 14 show configuration views of the reduced pressure chamber 7. In Fig. 12, the reduced pressure chamber 7 is configured by the first discharge electrode 11 and the second discharge electrode 12 of flat plates, and a dielectric 22. One of the first discharge electrode 11 and the second discharge electrode 12 is supplied with an AC voltage from the power source 50, and the other is superimposed with a DC voltage therefrom or grounded. The plasma 100 is generated at an area between the dielectric 22 and the second discharge electrode 12. When the dielectric 22 is made to be sufficiently larger than the first discharge electrode 11, it can be prevented that a discharge is generated between the first discharge electrode 11 and the second discharge electrode 12 without interposing the dielectric 22 therebetween.

[0041] In Fig. 13, the reduced pressure chamber 7 is configured by the first discharge electrode 11 and the dielectric 22 of flat plates, and an electrode 24 in a rod-like shape or a net-like shape as the second discharge electrode. Fig. 13 (b) is a view viewing from a direction b of (A). The first discharge electrode 11 is supplied with an AC voltage from the power source 50, and the electrode 24 is supplied with a DC voltage. In a converse case, the second discharge electrode 24 is supplied with an AC voltage from the power source 50 and the first discharge electrode 11 is supplied with a DC voltage. The electrode may be grounded instead of being supplied with a DC voltage. A plasma is generated at the region 100 between the dielectric 22 and the electrode 24. An ion, a low speed electron, or an excited state molecule which is generated at the region 100 of the plasma is diffused to an area of impinging on a sample molecule to thereby ionize the sample. The sample does not pass the plasma area having a high charged particle density. Therefore, although an efficiency of ionization becomes low, the sample is difficult to impinge on an electron having a high energy. Therefore, the fragmentation can be restrained.

[0042] In Fig. 14, the reduced pressure chamber 7 is configured by the dielectric 22 in a column-like shape, the first discharge electrode 11 which is brought into contact therewith, and the second discharge electrode 12 in a rod-like shape. A plasma is generated between the second discharge electrode 12 and the dielectric 22. When center axes of the second discharge electrode 12

and the dielectric 22 are shifted from each other, the discharge is started at a point at which a distance between the first discharge electrode 1 and the second discharge electrode is short. A discharge is started also at other area by charged particles generated at the point. Therefore, a voltage by which the discharge starts can be lowered.

[0043] In a case of carrying out an ionization in the reduced pressure chamber 7, a flow speed of the sample gas becomes smaller than that in a case of an ionization at inside of the capillary as in the first example. Therefore, an efficiency of the ionization by an ion-molecule reaction is increased. On the other hand, a volume of an area where the plasma is generated is increased. Therefore, an input power which is necessary for generating a plasma of the same density is increased.

Fifth Example

[0044] Fig. 15 is a configuring view showing a mass spectrometer according to a fifth example useful to understand the present invention. The configuration other than the ionization source is similar to that of the first example and an explanation thereof will be omitted. Also, the effect of the pressure at the area where the plasma 100 is generated, and the output voltage of the power source 50 are similar to those of the first example. A sample solution which is supplied to an ESI probe 30 is ionized by an electrospray ionization (ESI).

[0045] An ion and a charged droplet which are generated by the electrospray ionization are introduced to the dielectric capillary 10 by passing an inlet end electrode 31. The dielectric capillary 10 is heated to promote separation of a solvent molecule from the charged droplet. A neutral vapor and a portion of neutral molecules which are separated from the charged droplet which are introduced into the dielectric capillary 10 are ionized at a plasma ionization source portion 33. Ions which are generated by ESI and ions which are generated by the plasma ionization source portion 33 are extracted by passing an outlet end electrode and are introduced to an ion optics system at a later stage.

[0046] The ESI probe is applied with a voltage of about 1 through 10 kV in a case of measuring a positive ion and about -1 through -10 kV in a case of measuring a negative ion. When a voltage having a polarity inverse to that of an ion is superimposed on the inlet end electrode 31, the ion which is generated by ESI can be introduced to the capillary further efficiently. When a DC voltage is applied to the outlet end electrode 32, the ion is easy to be introduced to the ion optics system at the later stage.

[0047] According to the present embodiment, in comparison with a general ionization source of only electrospray ionization, a sample which has not been ionized by the electrospray ionization can be ionized by the plasma ion source 33. Therefore, a higher sensitivity is achieved. Also, even a molecule having a low polarity or an intermediate polarity which is difficult to be ionized by ESI in a plasma can directly be ionized.

[0048] When a temperature of a discharge gas is elevated by setting a voltage inputted to the power source 50 to be high during a time period other than a measurement time period, an impurity which is adhered to an inner wall of the dielectric capillary 10 can be removed by heating inside of the dielectric capillary 10 commonly to the other embodiments.

List of Reference Signs

[0049] 1 ... ionization source, 2 ... first differential pumping chamber, 3 ... second differential pumping chamber, 4 ... multipole ion guide, 5 ... mass spectrometry unit, 6 ... detector, 7 ... reduced pressure chamber, 10 ... dielectric capillary, 11 ... first discharge electrode, 12 ... second discharge electrode, 13 ... dielectric capillary, 14 ... first discharge electrode, 15 ... second discharge electrode, 20 ... orifice, 21 ... orifice, 22 ... dielectric, 24 ... discharge electrode, 30 ... ESI probe, 31 ... inlet end electrode, 32 ... outlet end electrode, 33 ... plasma ion source portion, 40 ... first discharge electrode, 41 ... second discharge electrode, 42 ... insulator, 50 ... ionization source power supply, 51 ... vacuum pump, 52 ... vacuum pump, 53 ... vacuum pump, 100 ... plasma

Claims

1. A mass spectrometer comprising:

a first electrode (13);
a second electrode (12);
a dielectric portion (10) provided between the first electrode (13) and the second electrode (12) and having an introducing portion and an extracting portion for a sample;
a power source (50) for superimposing an alternating current voltage on one of the first electrode (13) and the second electrode (12) and ionizing the sample by a discharge generated between the first electrode (13) and the second electrode (12); and
a mass analyzing portion (5) for analyzing an ion extracted from the extracting portion,
wherein the discharge is carried out at 2 Torr (2.7×10^2 Pa) or higher and 300 Torr (400×10^2 Pa) or lower,
wherein the dielectric portion (10) is configured by a shape of a cylinder, and the second electrode (12) is provided at an outside of the cylinder,
characterized in that the first electrode (13) is formed as a conductor capillary which is connected to the sample extracting portion of the dielectric portion (10).

2. The mass spectrometer according to claim 1, where-

in the discharge is carried out at 4 Torr (5.3 x 10^2 Pa) or higher.

3. The mass spectrometry according to claim 1, wherein the discharge is carried out at 7 Torr (9.3 x 10^2 Pa) or higher.

4. The mass spectrometer according to claim 1, wherein the discharge gas is air.

5. The mass spectrometer according to any preceding claim, wherein the power source (50) is adapted to superimpose the alternating current voltage at a frequency equal to or higher than 1 kHz and equal to or lower than 300 kHz.

6. The mass spectrometer according to claim 5, wherein the frequency is equal to or higher than 1 kHz and equal to or lower than 20 kHz.

7. The mass spectrometer according to any preceding claim, further comprising:

an electrospray ionization probe (30) for generating a charged droplet and an ion of a sample solution on a side of the introducing portion of the sample;
wherein the dielectric portion (10) is heated.

Patentansprüche

1. Massenspektrometer mit
einer ersten Elektrode (13),
einer zweiten Elektrode (12),
einem dielektrischen Abschnitt (10), der zwischen der ersten Elektrode (13) und der zweiten Elektrode (12) vorgesehen ist und einen Einleitabschnitt und einen Ausleitabschnitt für eine Probe aufweist,
einer Leistungsquelle (50) zum Überlagern einer Wechselstromspannung auf die erste Elektrode (13) oder die zweite Elektrode (12) und zum Ionisieren der Probe durch eine zwischen der ersten Elektrode (13) und der zweiten Elektrode (12) erzeugten Entladung, und
einem Massenanalyseabschnitt (5) zum Analysieren eines aus dem Ausleitabschnitt extrahierten Ions,
wobei die Entladung bei mindestens 2 Torr (2,7 x 10^2 Pa) und höchstens 300 Torr (400 x 10^2 Pa) durchgeführt wird,
wobei der dielektrische Abschnitt (10) durch eine Form eines Zylinders konfiguriert ist, und die zweite Elektrode (12) an einer Außenseite des Zylinders vorgesehen ist,
dadurch gekennzeichnet, dass die erste Elektrode (13) als eine Leitungskapillare ausgebildet ist, die an den Probenausleitabschnitt des dielektrischen Abschnitts (10) angeschlossen ist.

2. Massenspektrometer nach Anspruch 1, wobei die Entladung bei mindestens 4 Torr (5,3 x 10^2 Pa) durchgeführt wird.

3. Massenspektrometer nach Anspruch 1, wobei die Entladung bei mindestens 7 Torr (9,3 x 10^2 Pa) durchgeführt wird.

4. Massenspektrometer nach Anspruch 1, wobei das Entladungsgas Luft ist.

5. Massenspektrometer nach einem der vorstehenden Ansprüche, wobei die Leistungsquelle (50) dazu ausgelegt ist, die Wechselstromspannung bei einer Frequenz von mindestens 1 kHz und höchstens 300 kHz zu überlagern.

6. Massenspektrometer nach Anspruch 5, wobei die Frequenz mindestens 1 kHz und höchstens 20 kHz beträgt.

7. Massenspektrometer nach einem der vorstehenden Ansprüche, ferner mit
einer Elektrospray-Ionisierungssonde (30) zum Erzeugen eines geladenen Tröpfchens und eines Ions einer Probenlösung auf einer Seite des Probeneinleitabschnitts,
wobei der dielektrische Abschnitt (10) geheizt wird.

Revendications

1. Spectromètre de masse comprenant :

une première électrode (13) ;
une deuxième électrode (12) ;
une partie diélectrique (10) prévue entre la première électrode (13) et la deuxième électrode (12) et ayant une partie d'introduction et une partie d'extraction pour un échantillon ;
une source d'alimentation électrique (50) pour superposer une tension de courant alternatif sur une de la première électrode (13) et de la deuxième électrode (12) et ioniser l'échantillon par une décharge générée entre la première électrode (13) et la deuxième électrode (12) ; et
une partie d'analyse de masse (5) pour analyser un ion extrait de la partie d'extraction,
dans lequel la décharge est exécutée à 2 Torr (2,7 x 10^2 Pa) ou plus et 300 Torr (400 x 10^2 Pa) ou moins,
dans lequel la partie diélectrique (10) est configurée par une forme d'un cylindre, et la deuxième électrode (12) est prévue au niveau d'un extérieur du cylindre,
caractérisé en ce que la première électrode

(13) est formée comme un capillaire conducteur qui est connecté à la partie d'extraction d'échantillon de la partie diélectrique (10).

2. Spectromètre de masse selon la revendication 1, dans lequel la décharge est exécutée à 4 Torr (5,3 x 10^2 Pa) ou plus.

3. Spectromètre de masse selon la revendication 1, dans lequel la décharge est exécutée à 7 Torr (9,3 x 10^2 Pa) ou plus.

4. Spectromètre de masse selon la revendication 1, dans lequel le gaz de décharge est l'air.

5. Spectromètre de masse selon une quelconque revendication précédente, dans lequel la source d'alimentation électrique (50) est adaptée à superposer la tension de courant alternatif à une fréquence égale ou supérieure à 1 kHz et égale ou inférieure à 300 kHz.

6. Spectromètre de masse selon la revendication 5, dans lequel la fréquence est égale ou supérieure à 1 kHz et égale ou inférieure à 20 kHz.

7. Spectromètre de masse selon une quelconque revendication précédente, comprenant en outre :

une sonde d'ionisation par électronébulisation (30) pour générer une gouttelette chargée et un ion d'une solution échantillon sur un côté de la partie d'introduction de l'échantillon ;
dans lequel la partie diélectrique (10) est chauffée.

FIG. 1

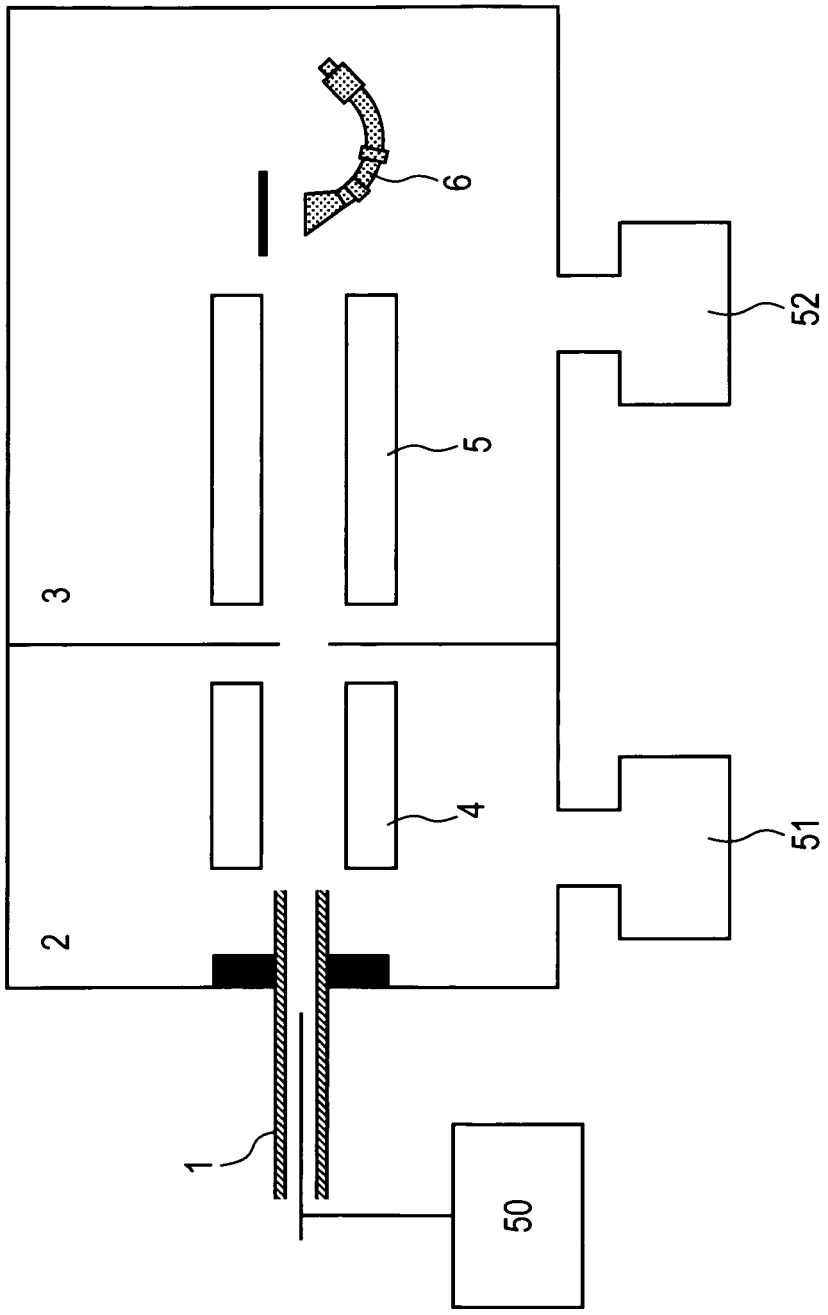


FIG. 2B

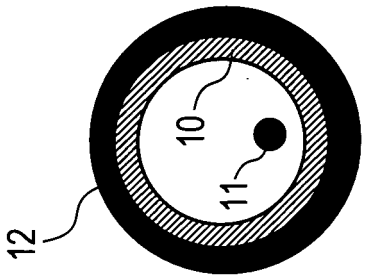


FIG. 2A

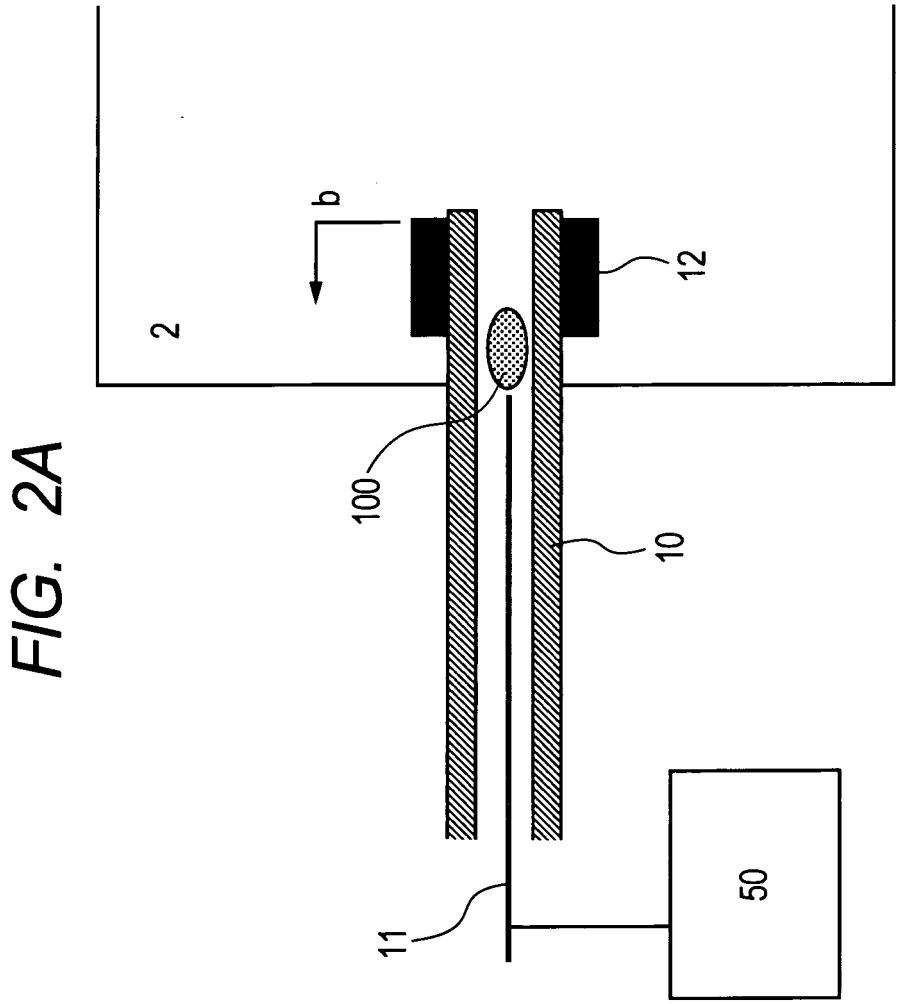


FIG. 3

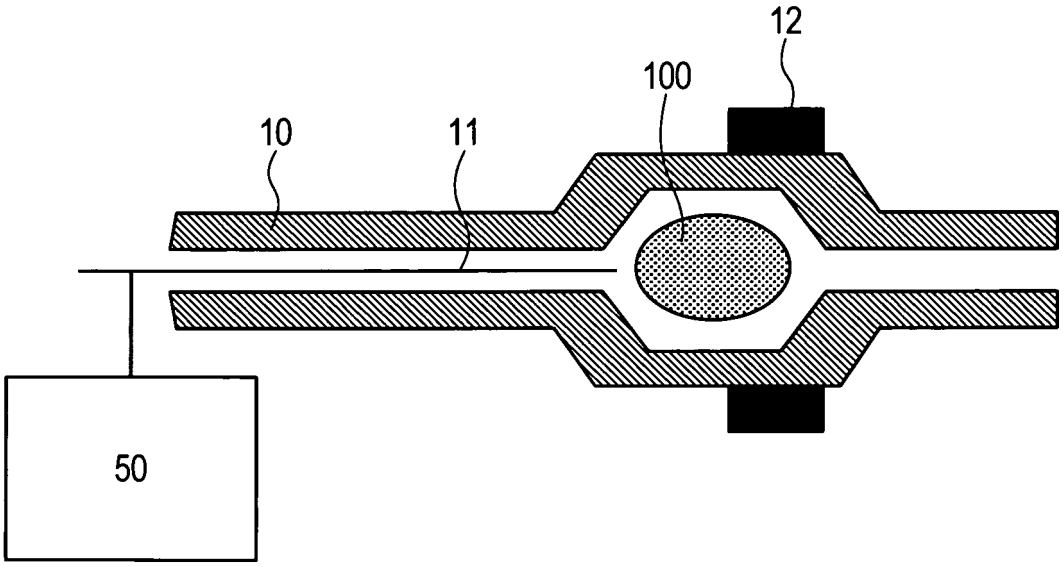


FIG. 4B

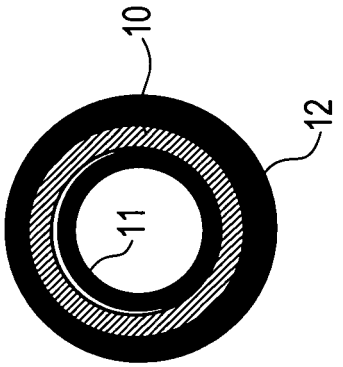


FIG. 4A

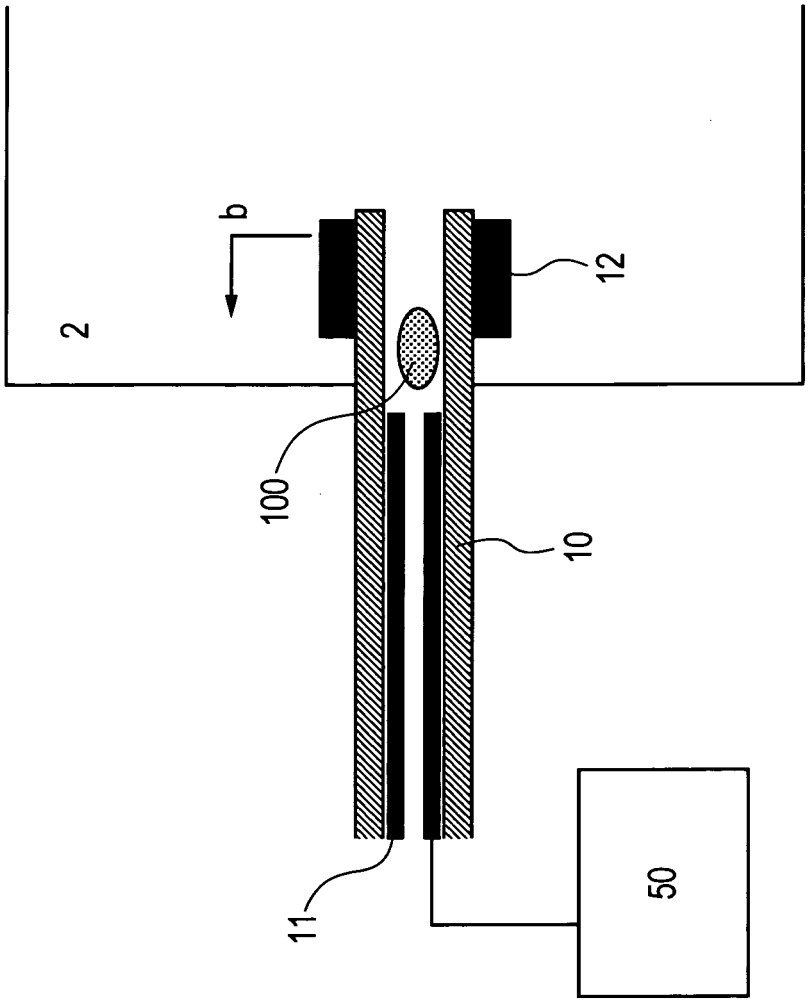


FIG. 5

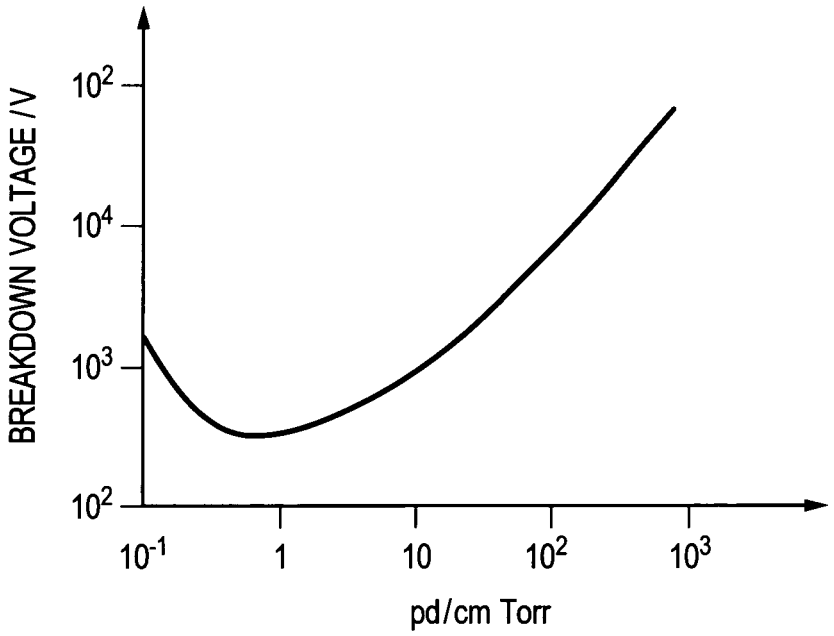


FIG. 6

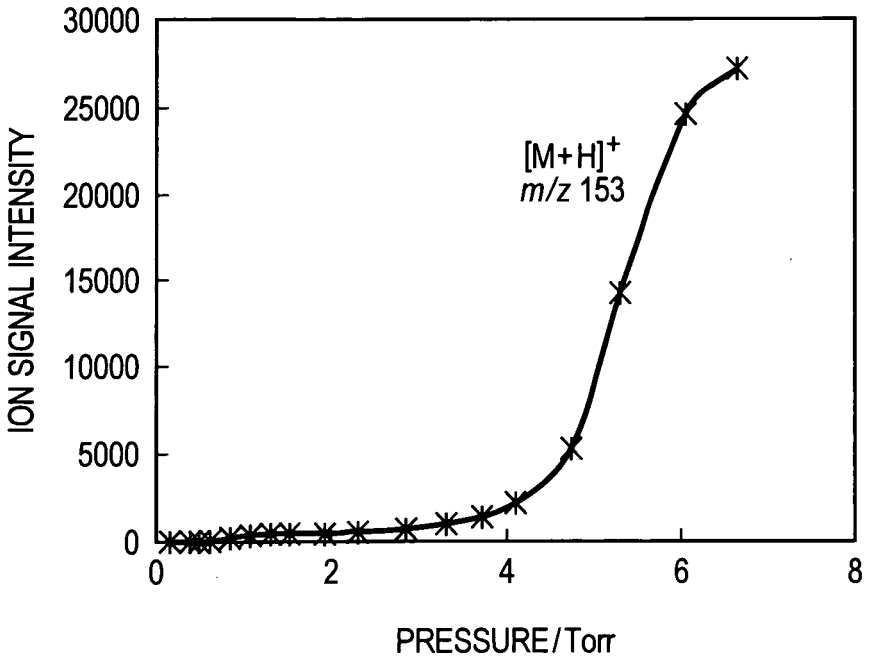

30000
25000
20000
15000
10000
5000
0
ION SIGNAL INTENSITY
[M+H]+
m/z 153
0
2
4
6
8
PRESSURE/Torr

FIG. 7

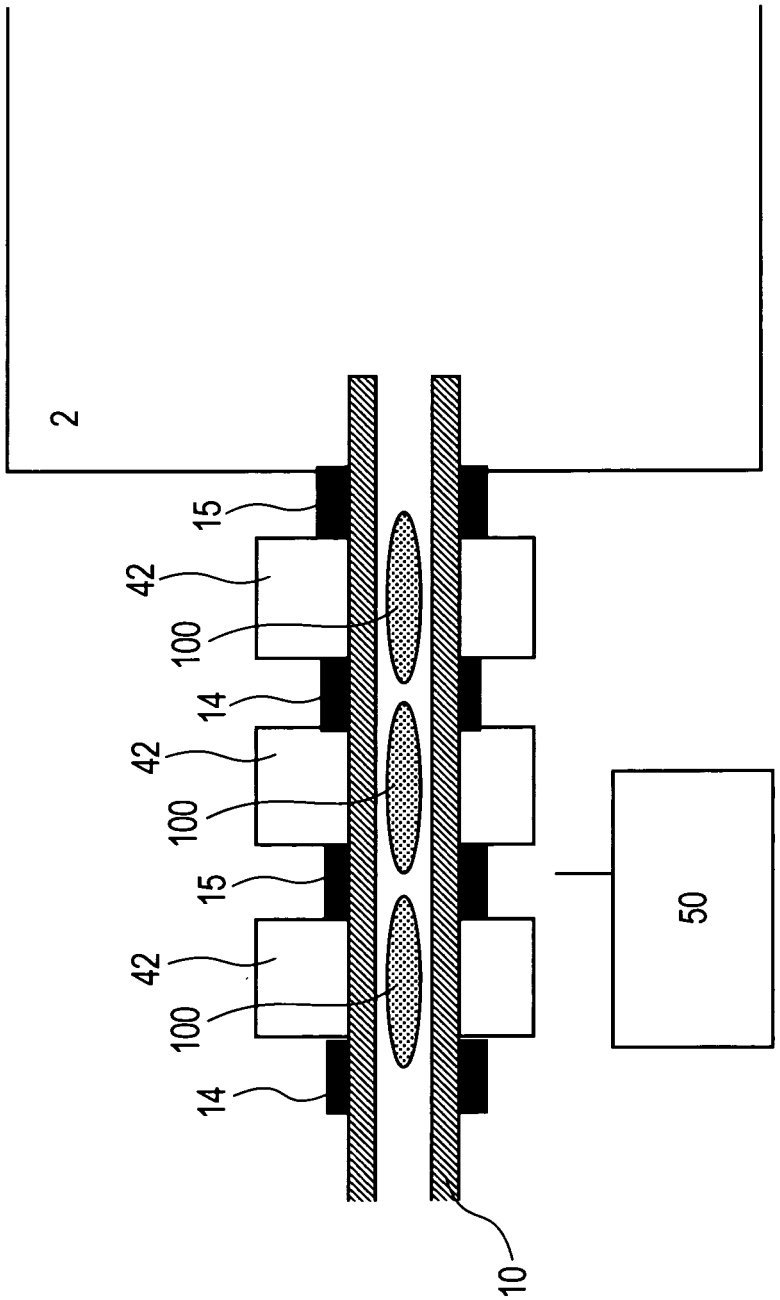


FIG. 8

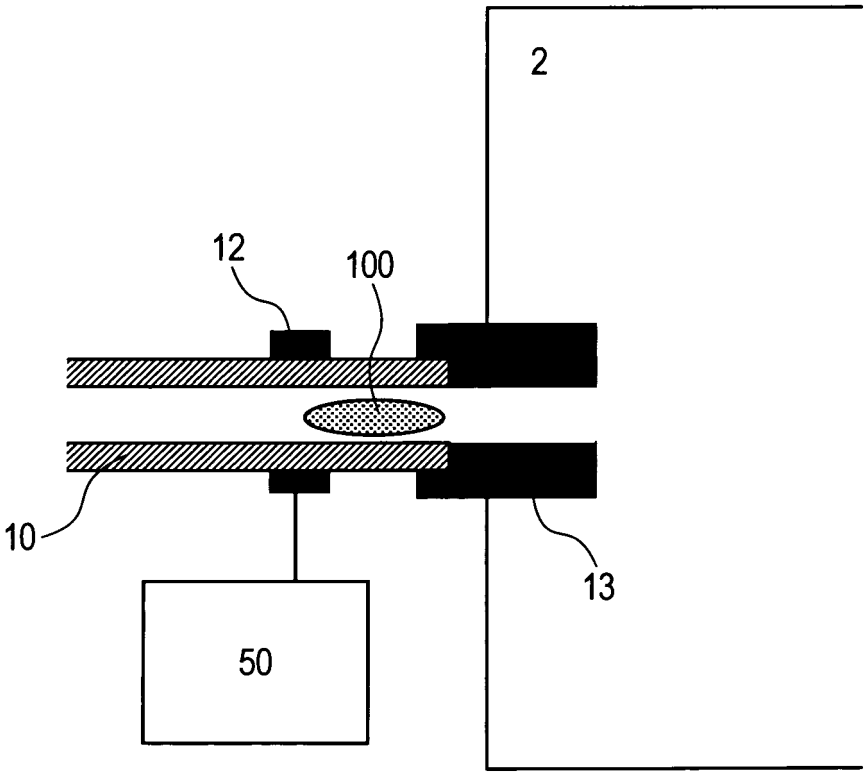


FIG. 9B

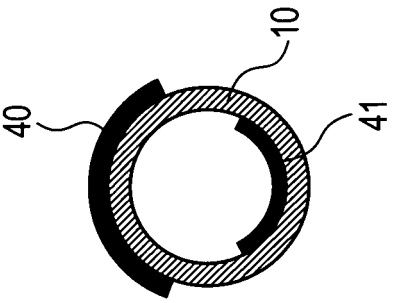


FIG. 9A

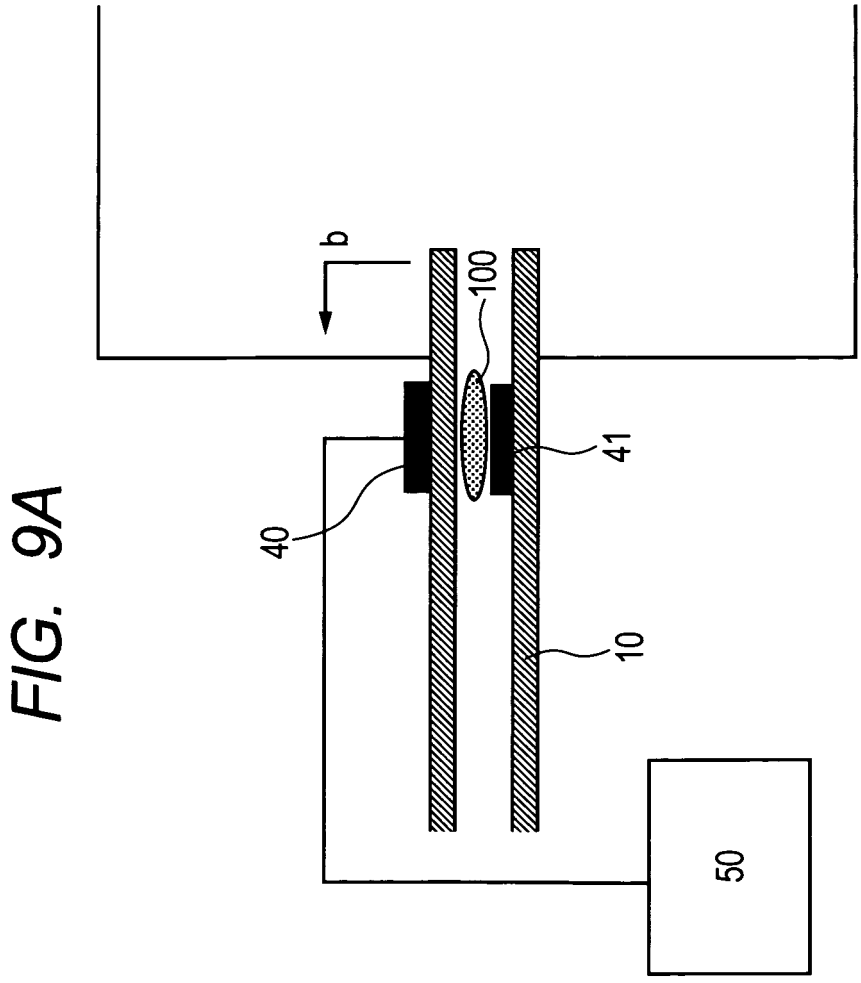


FIG. 10B

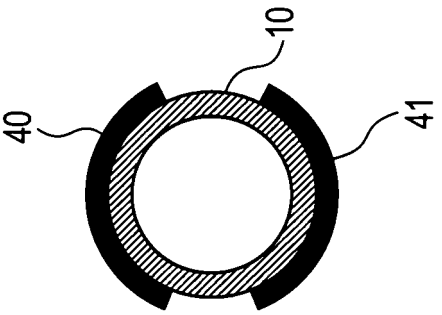


FIG. 10A

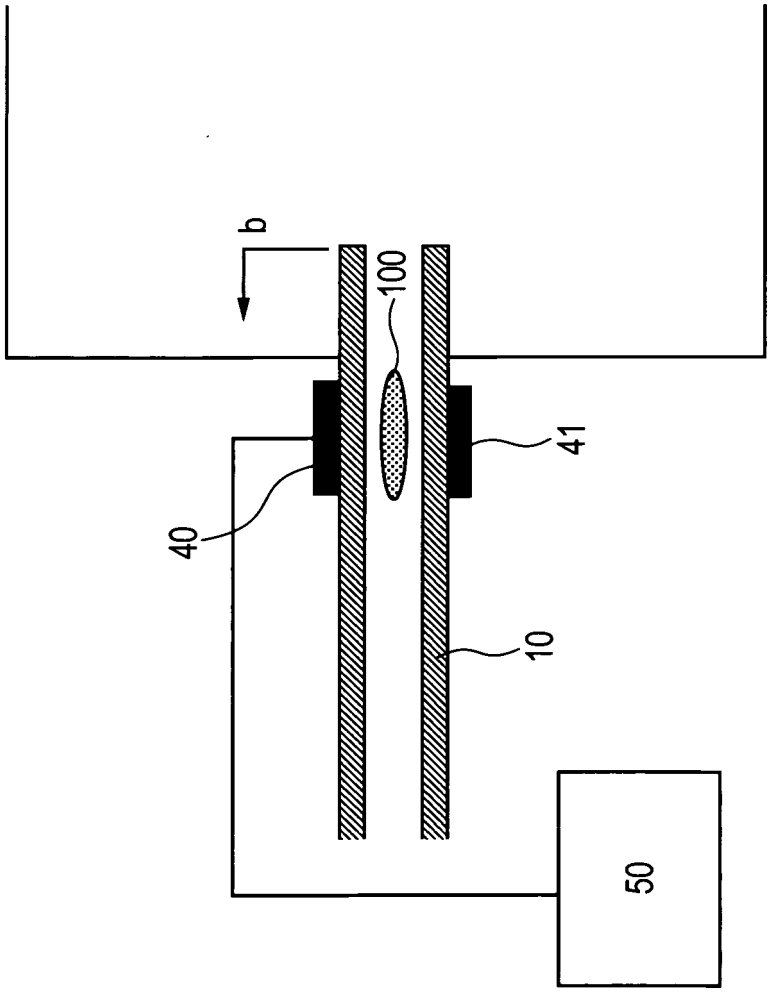


FIG. 11

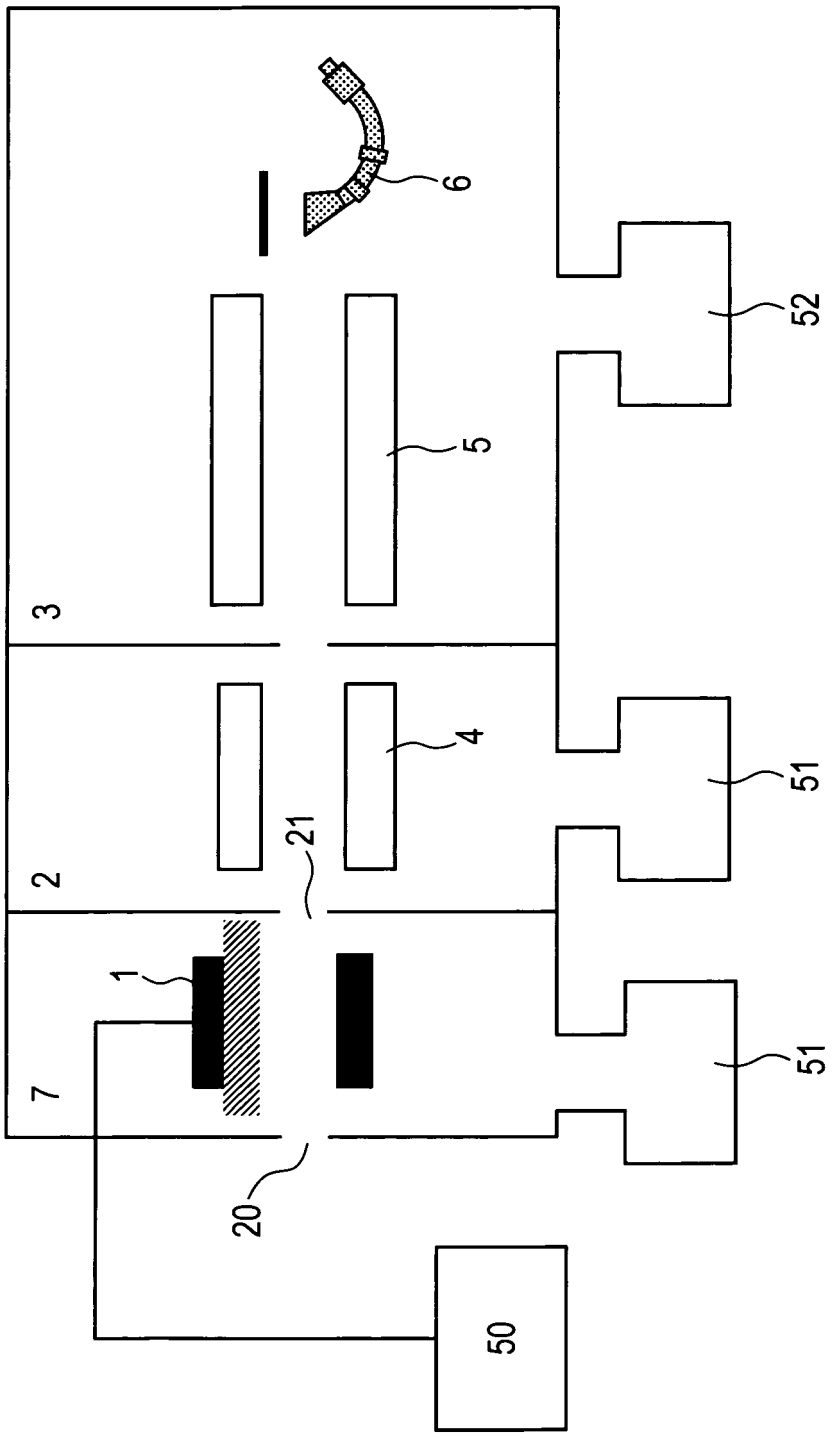


FIG. 12B

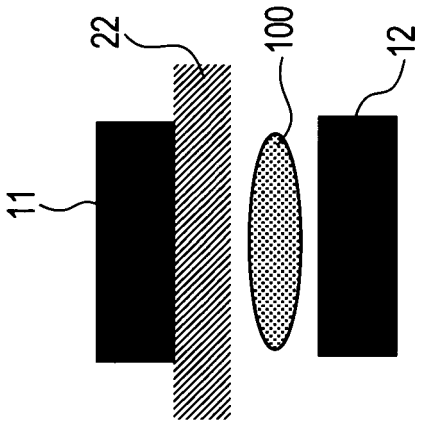


FIG. 12A

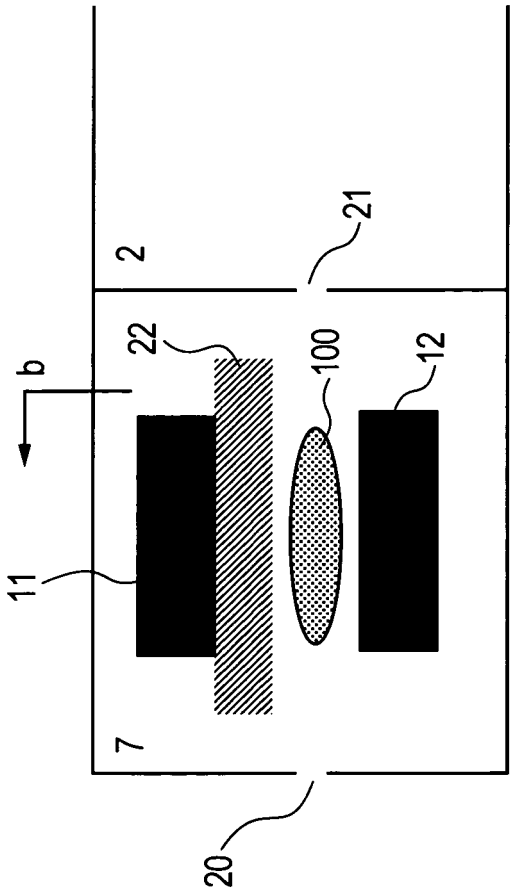


FIG. 13B

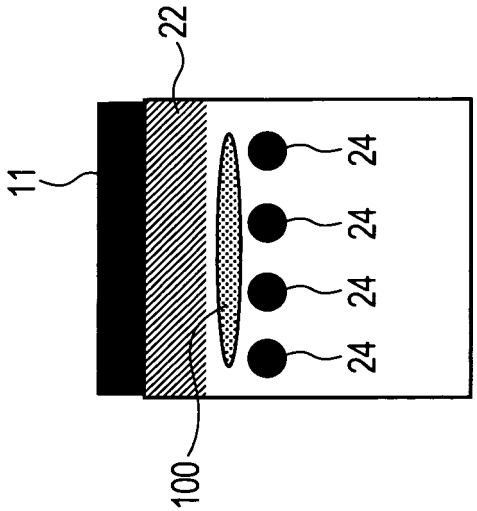


FIG. 13A

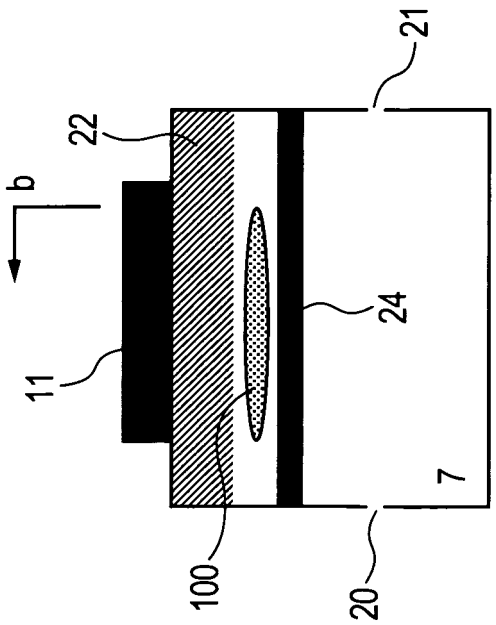


FIG. 14B

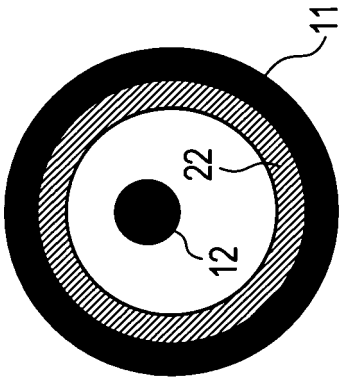


FIG. 14A

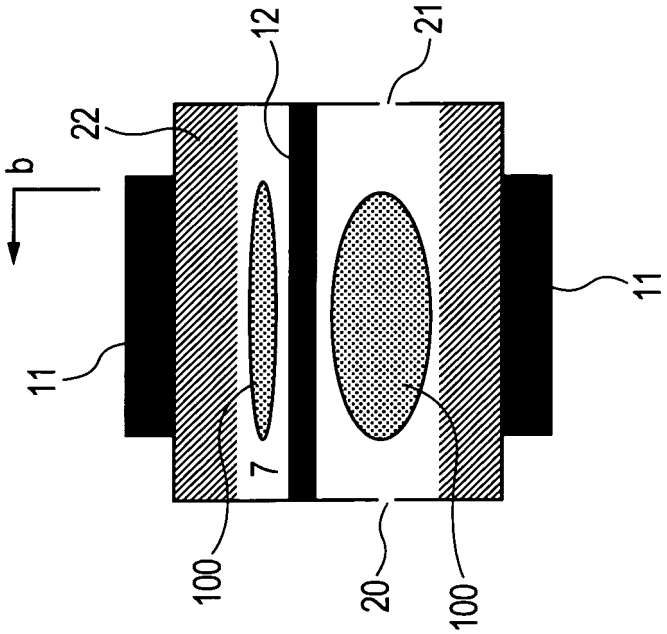
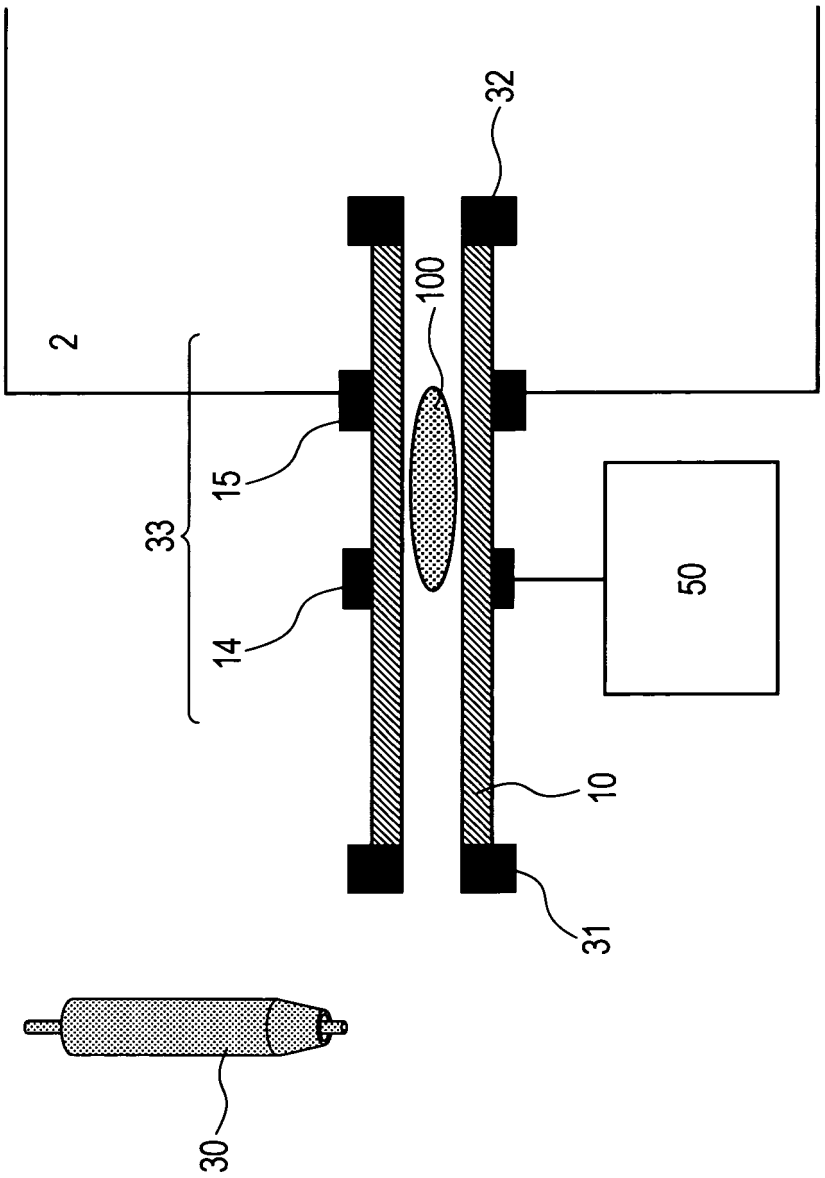


FIG. 15



REFERENCES CITED IN THE DESCRIPTION

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- US 4849628 A **[0007]**
- WO 2009102766 A **[0007]**
- US 2005121607 A1 **[0008]**

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- *Analytical chemistry,* 1998, vol. 70, 513-518 **[0009]**